Static and dynamical dipolar / strain fluctuations in perovskite ferroelectric relaxors

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We develop a theory to study the characteristics of dipolar / strain fluctuations in perovskite relaxors. In addition to the soft TO and TA phonons, we take into account another freedom of motion associated with the random hopping of Pb^{2+} ions between the off-center sites around the high symmetry corner site, thus constructing a coupled TO-TA-pseudospin model to describe the perovskite relaxors. It is shown that there is a possibility that prior to the on-set of instability of the uniform TO-mode (soft-mode), instability of TA mode with nanometer scale modulation ($\mathbf{q} \sim 0.1\mathbf{a}^*$) takes place, which produces static heterogeneous structure concerning polarization as well as shear strain. This seems to suggest the intrinsic origin of the heterogeneity in relaxors visualized as random distribution of PNR. The phonon spectral density distribution has also been investigated. It is shown that when the relaxation time of random hopping of Pb^{2+} ions is comparable to the TO phonon frequency at $\mathbf{q} \sim 0.1\mathbf{a}^*$, the calculated phonon spectral density reproduces the characteristic features called 'waterfall'.

I. INTRODUCTION

Recently, the unique properties of ferroelectric relaxors have become one of the central topics in solid state physics. The diffuseness of the dielectric response against temperature variation has been considered to be due to the randomness of the system created by the random occupation of B-site ions with different valences. In fact, the basic physics of relaxors has been mainly discussed in terms of 'random field' to stabilize a glassy state analogous to spin glasses.

One of the intriguing problems to be answered is the role of Pb^{2+} -ions on A-site. In spite of the efforts to eliminate Pb ion based on technological reasons, hitherto known perovskite relaxors seem to be restricted to Pb compounds, which suggests that at least part of the unique properties would be related to Pb ions at A-site.

From experimental view point, there exist a few unique features exhibited by relaxors both in structural as well as lattice dynamical aspects providing some 'key concepts' to describe characteristic features of relaxors. The key concept to discuss the static structure of relaxors is the so-called PNR (polar nanoregion). That is, the averaged cubic symmetry is locally broken in the temperature region where dielectric constant exhibits broad maximum. The overall structure is thus visualized as a random distribution of PNR embedded on cubic parent phase.

We notice that there are a few materials which show similar intrinsic heterogeneity in the vicinity of phase transition point. A group of bcc-based alloys called shape memory alloys, which undergo martensitic transformation, exhibit heterogeneous structure where the 'embryo's or microdomains of martensite are embedded on the austenite (bcc) matrix over a wide temperature range. More recently, a group of perovskite manganites called CMR substances, which undergo metal-insulator transition, have been noticed to develop heterogeneous structure[1] where microdomains of metallic phase are coexisting with insulator phase. The close relationship between CMR substances and relaxors was already pointed out by Kimura et al.[2]

Onuki[3] investigated the origin of the stability of two-phase coexistence in alloys and pointed out that the coupling between the order parameter to the local strain is essential to stabilize the heterogeneous structure. Later, Yamada and Takakura[4] also arrived at the same conclusion in the case of CMR substances.

In this connection, the recent neutron scattering study on PMN by Hirota et al.[5] seems to be very suggestive. They carried out the dynamical structure analysis of the diffuse scattering and concluded that the displacement pattern of each ion in the unit cell contains considerable amount of CM (center of mass) non-conserving components. In the language of phonon modes, it means that the normal coordinate of the condensing mode is given by a linear combination of TO-mode and TA-mode suggesting the possibility of strong polarization-strain coupling.

On the other hand, the key concept to characterize the dynamical aspect of relaxors is so-called 'waterfall' in phonon spectrum. Gehring et al.[6] carried out the pioneering neutron scattering study on PZN-8PT and found out that the observed high intensity ridge of the neutron spectrum did not follow the expected TO phonon dispersion at $q \leq 0.2\mathbf{a}^*$. Instead, it falls down vertically to precipitate onto TA dispersion. Similar features are successively observed in various relaxors including PMN and PZN,[7,8,9] indicating that waterfall is indeed the unique lattice dynamical characteristic of relaxors.

Gehring et al.[10] analyzed the neutron spectrum of PZN based on the 'mode coupling' treatment which was utilized by Harada et al.[11] to explain the phonon spectrum of $BaTiO_3$. They concluded that in order to reproduce the observed spectrum, the TO phonon width should show an abrupt change at $q \sim 0.1a^*$ where waterfall takes place. They claim that the abrupt change is caused by the random distribution of PNR in the medium, thereby the propagation of the lattice wave with wave length longer than the average size of PNR is impeded. While

this viewpoint is very attractive, whether the static heterogeneity such as PNR will cause waterfall type anomaly or not is unclear since a static entity will only give rise to large momentum transfer of the phonon without causing any energy transfer from phonons to other freedom of motion and eventually to heat bath. In order to establish effective channels of energy transfer, some dynamical entity to which phonons are coupled would be needed.

We consider that the configurational freedom of motion of Pb^{2+}-ion will provide such possibility. It is known[12] that in relaxors the instantaneous equilibrium position of Pb^{2+} ion is slightly shifted from the high symmetry corner site and is making random hopping motion between the equivalent off-center sites to recover cubic symmetry on average. Formally, such freedom of motion can be expressed by a stochastic pseudospin variable. Based on these considerations we construct a suitable model of the relaxor which is characterized by 'coupled TO-TA-pseudospin system'. In the next section, we discuss the TO-TA coupling within the framework of 'quasi-harmonic' approximation which was utilized by Axe, Harada and Shirane (AHS)[13] in order to analyze the anomalous TA dispersion in $KTaO_3$. When applied to PMN, this treatment suggests the possibility to stabilize a heterogeneous static structure. In section 3, we discuss the neutron scattering spectra including waterfall anomaly by taking into account of random hopping of Pb^{2+} ions. The last section is devoted to conclusions and discussions.

II. STATIC POLARIZATION / STRAIN FLUCTUATIONS – ORIGIN OF POLAR NANOREGION –

According to the analysis of the diffuse scattering intensities observed in PMN around various reciprocal lattice points by Hirota et al.,[5] the structure factor of the condensing mode includes substantial amount of atomic displacements which does not conserve the center of mass (CM) of the unit cell. Since the optical modes at $q = 0$ should satisfy the condition of CM-conservation of the coordinates, the above observation seems to suggest that in PMN, there would be strong coupling between the soft optical mode and the transverse acoustic mode around $q = 0$, so that the normal coordinates include considerable amount of CM-nonconserving displacements. In this connection, we notice that there are a few perovskite ferroelectric materials, which exhibit anomalous behavior in the TA branch upon softening of the TO branch. Fig. 1 shows typical behavior in the case of $KTaO_3$.[14] It is seen that as the TO mode softens, the dispersion of the TA branch exhibits anomalous 'concave' curve in a limited q-region of $0.02 \le q \le 0.2$. It is noticeable that the dispersion shows no 'softening' in the vicinity of the reciprocal lattice point within $q \le 0.02$. Such anomaly in the TA dispersion also indicates the possibility of strong coupling between TO- and TA- modes in perovskite ferroelectric systems.

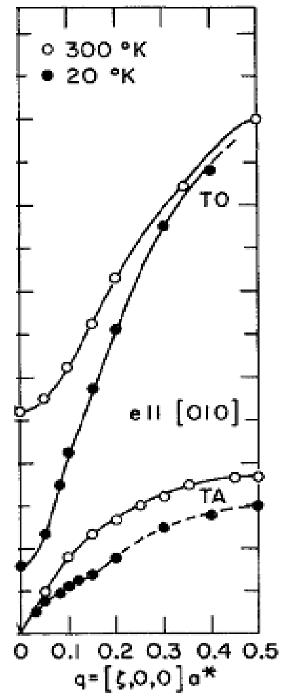

FIG. 1: The TO and TA phonon dispersions of $KTaO_3$ at 300K and 20K given in ref. 14. As the TO branch 'softens' upon lowering temperature, the TA branch exhibits anomalous concave curve in a limited q-region of $0.02 \le q \le 0.25$. Notice the dispersion shows no anomaly in the direct vicinity of the zone center ($q = 0$) within $q \le 0.02$.

In 1970, Axe et al.[13] discussed the anomalous behavior of TA branch in $KTaO_3$ in the framework of 'quasi-harmonic coupling' treatment. They express the dynamical matrix $\mathbf{D}(\mathbf{q})$ of the harmonic potential by taking the normal coordinates at $q = 0$ as the basis functions. The off-diagonal matrix elements $D_{ij}(q)$ may then be considered as the mode-mode coupling energy between the i'th and j'th modes. By taking only TA-TO coupling into account the phonon properties (characteristic frequency and the corresponding normal coordinates) are explicitly given by solving the following secular equation:

$$\begin{vmatrix} \omega_0^2(T) + F_{11}(\mathbf{q}) - \omega^2(\mathbf{q}) & F_{12}(\mathbf{q}) \\ F_{21}(\mathbf{q}) & F_{22}(\mathbf{q}) - \omega^2(\mathbf{q}) \end{vmatrix} = 0, \qquad i \begin{cases} = 1 : \mathrm{TO} \\ = 2 : \mathrm{TA} \end{cases} \tag{1}$$

where $\omega_0(T)$ is the soft mode frequency at $q = 0$ which is the only temperature dependent quantity. $F_{ij}(\mathbf{q})$ are to be expanded in terms of $\mid \mathbf{q} \mid$ as:

$$F_{ij}(\mathbf{q}) = f_{ij}^{(2)}(\boldsymbol{\kappa}) q^2 + f_{ij}^{(4)}(\boldsymbol{\kappa}) q^4, \tag{2}$$

$$\boldsymbol{\kappa} = \mathbf{q}/\mid \mathbf{q} \mid, \tag{3}$$

along a specific direction $\boldsymbol{\kappa}$. The diagonal elements $f_{ij}^{(v)}(\boldsymbol{\kappa})$'s may be obtained by comparing with the experimental dispersion curves at high temperatures where no anomaly is observed. In particular, $f_{22}^{(2)}(\boldsymbol{\kappa})$ is directly given by the elastic constant for shear strain along $\boldsymbol{\kappa}$-direction. The only essential parameters to be fixed are $f_{ij}^{(v)}$'s with $i \neq j$ describing the coupling between TO- and TA- modes. Axe et al.[13] analyzed the experimental results on $KTaO_3$ and successfully reproduced the TA, as well as TO, dispersions at various temperatures by fitting these two parameters.

We further notice that the off-diagonal matrix elements of the transformation matrix of the basis functions, $\mathbf{S}(\mathbf{q})$, become comparable to the diagonal ones in the q-region where the TA branch exhibits anomalous behavior. For instance, $\mathbf{S}(\mathbf{q})$ at $\mathbf{q} = (0, 1, 0, 0)$ in $KTaO_3$ is given by,

$$\mathbf{S}(0.1, 0, 0) = \begin{pmatrix} 0.880 & 0.475 \\ -0.475 & 0.880 \end{pmatrix}. \tag{4}$$

This means that in the q-region where anomaly in TA dispersion takes place the normal coordinate of TO-mode contains large amount of uniform translational displacements, and vice versa. (TA-mode contains large amount of pure optical displacements.) This behavior reminds us the characteristics of the dynamical structure factors as pointed out by Hirota et al. in the case of PMN.

It is noticeable that $PbTiO_3$, the prototype material of perovskite relaxors, was reported[15] to exhibit the same type anomaly in TA dispersion. Therefore, it would not be unreasonable to assume that perovskite relaxors also belong to the materials which experience strong TO-TA coupling. Unfortunately, such anomaly can not be proved directly by the observation of neutron spectra in relaxors because of the extraordinarily large damping characterized by the 'waterfall' phenomena.

At this stage, we try to construct the 'hypothetical' dispersion curves of PMN within the 'quasi-harmonic' coupling formalism by completely neglecting the anharmonicity of the potential to cause damping. Among the parameters defined in eq. (2), $f_{22}^{(2)}(\boldsymbol{\kappa})$ is unambiguously given by the observed elastic constants c_{44} and $1/2(c_{11} - c_{12})$ for $\boldsymbol{\kappa}$ // [100] and $\boldsymbol{\kappa}$ // [110] respectively.[16] The remaining $f_{ij}^{(v)}(\boldsymbol{\kappa})'$s are assumed to be isotropic (independent of $\boldsymbol{\kappa}$) and to take the same values as those for $KTaO_3$ given by Axe et al..

The results of calculation are given in Fig. 2. The dispersion of TA [100] shows the expected concave curve. In contrast, the dispersion of TA [110] exhibits a 'dip' around $q \sim 0.1$. Moreover, by subtle adjustment of the parameters, the dip becomes more pronounced so that $\omega_{TA} \rightarrow 0$ at $q = 0.12$. That is, the TA mode has become 'condensed' to form a modulated static structure with modulation period $\lambda_0 = 2\pi/q_0 = \frac{a}{0.12}$.

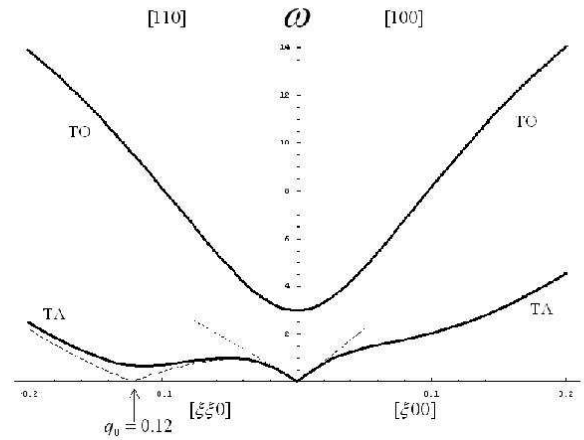

FIG. 2: The calculated 'hypothetical' phonon dispersions in PMN. The dashed lines are the asymptotic behavior at $q \simeq 0$ determined by the observed elastic constants[15] along [100] and [110]-directions. The dotted curve corresponds to the case when the coupling parameters are slightly modified from the values determined for $KTaO_3$.

The transformation matrix at $q_0 = 0.12$ is calculated to give

$$S(0.12, 0.12, 0) = \begin{pmatrix} 0.895 & 0.445 \\ -0.445 & 0.895 \end{pmatrix}. \tag{5}$$

Therefore the local structure of the condensing TA mode is expressed as the linear combination of uniform translational and pure optical displacements with the ratio of $S_{21}/S_{22} = 0.50$.

Physically, this implies that the TA [110] mode with the wave length of nanometer order, λ_0, has the tendency to become unstable prior to the condensation of the uniform ($q = 0$) TO-mode due to the quasiharmonic coupling. Hence the system eventually stabilizes a polarization / strain modulated structure with wave length λ_0. As has been pointed out, such characteristics of the phonon dispersions are not able to be observed by inelastic neutron scattering experiment obscured by the large damping. On the other hand, X- ray diffuse scattering intensity, which is proportional to the instantaneous correlation of fluctuations, seems to give some indirect information on the characteristic frequency $\omega(\mathbf{q})$.

The X-ray intensity due to the excitation of the phonons belonging to λ'th branch is given, irrespective of the property of damping,[17] as

$$I^{\lambda}(\mathbf{K}) = \frac{1}{\omega_{\lambda}^{2}(\mathbf{q})} \mid F_{\lambda}(\mathbf{K}) \mid^{2}, \tag{6}$$

where $F^{\lambda}(\mathbf{K})$ is the dynamical structure factor of the λ'th mode. In the present system, where TA-mode, rather than TO, is assumed to become extremely soft, we may

express the X-ray diffuse intensity around each Bragg point, $\mathbf{K}_h$, in the form:

$$I(\mathbf{K}) \cong \frac{1}{\omega_{TA}^2(\mathbf{q})} \mid F_{TA}(\mathbf{K}) \mid, \tag{7}$$

$$F_{TA}(\mathbf{K}) \cong S_{22}F_{TA}^0(\mathbf{K}_h) + S_{21}F_{TO}^0(\mathbf{K}_h), \tag{8}$$

where $F_{TA}^0(\mathbf{K}_h)$ and $F_{TO}^0(\mathbf{K}_h)$ are the dynamical structure factors for the pure translational, and pure optical displacements at $q = 0$ respectively. Fig. 3(a) shows the calculated X-ray diffuse scattering intensity distributions around three Bragg positions in comparison with the observed X-ray results by You et al.. (Fig. 3(b)).[18] While overall characteristics of anisotropic distribution are reproduced qualitatively, a remarkable discrepancy is seen in the diffuse pattern around (400). The observed distribution does not show any clear existence of 'satellites' which are shown in the calculated contour. This point will be discussed later.

Although it is not shown explicitly in the figure, the relative intensities of the diffuse pattern reflects the degree of mixing of the modes, through the structure factors. Hirota et al.[5] gave the relative displacement for each ions in the unit cell which are divided into CM-conserving (TO-like) and CM-nonconserving (TA-like) components (See eq. (6) in ref. 5). Using the table, the experimental value of S_{21}/S_{22} is obtained as 0.63, which should be compared with the calculated value of 0.50 (See eq. (5)).

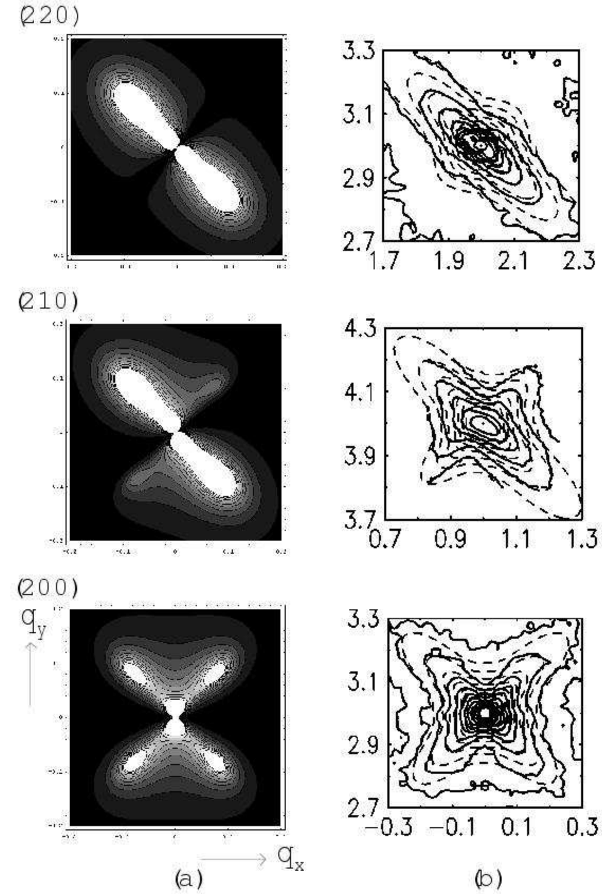

FIG. 3: (a) Calculated X-ray diffuse intensity distributions around various types of Bragg reflections, which are compared with the observed intensity distributions by You et al.[18] reproduced in (b).

III. DYNAMICAL POLARIZATION / STRAIN FLUCTUATIONS –ORIGIN OF WATERFALL–

The neutron spectrum of PMN along [100] in the temperature region where 'waterfall' phenomenon takes place has been analyzed by Gehling et al.[10] based on the coupled mode treatment utilized by Harada et al. to discuss the asymmetric spectra in $BaTiO_3$. In this treatment, there are five adjustable parameters to be fitted to the observed neutron intensity profile for each $\mathbf{q}$-value. It has been shown that, in order to reproduce the entire intensity distribution in the observed q-range, the effective width of TO-mode, $\Gamma_1(q)$, changes abruptly at $\mathbf{q}_0$ where 'waterfall' takes place. They claim that the abrupt increase of Γ_1 would be caused by inhomogeneity of the lattice due to random distribution of PNR with characteristic size of $\sim q_0^{-1}$.

While this interpretation is very attractive, the basis of the 'coupled mode' formalism on which the treatment is based, is a 'homogeneous anharmonic lattice'. The damping of phonons are caused by the energy flow to the heat bath through anharmonic potential, whence the static heterogeneity of the medium would be out of the framework of the treatment.

We take somewhat different standpoint. Besides the phonon system, we introduce a stochastic variable whose dynamical behavior is only statistically determined. When such variable is strongly coupled to phonons, the life time of phonons would be mainly determined by the energy flow to the heat bath through the random variable. In perovskite relaxors, the configurational freedom of Pb^{2+} ions seems to play the role of such stochastic variable since it is well established[12] that the instantaneous equilibrium position of Pb^{2+} ion is slightly displaced from the corner site due to covalency effect, and it is randomly hopping across the potential barrier between the equivalent off-centered sites allowed by the averaged cubic symmetry m3m. We may describe this freedom of motion of Pb^{2+} ion by a pseudospin which takes on a few distinct values. Thus, our standpoint is schematically envisaged as illustrated in Fig.4.

As the suitable framework to treat the coupled TO-TA-pseudospin system, we utilize Langevin equation which describes the motion of the variable under random force $\mathbf{f}(t)$,

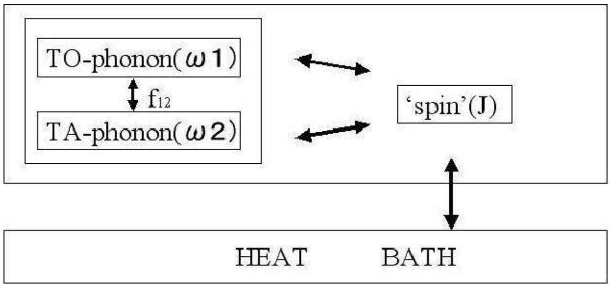

FIG. 4: Schematic description of the coupling scheme in TO-TA-pseudospin model. Major energy flow from the phonon system to heat bath is caused through the coupling to the pseudospin system.

$$\dot{\mathbf{A}}(t) = \mathbf{\Omega} \cdot \mathbf{A} - \int \mathbf{\Phi}(t-t') \cdot \mathbf{A}(t')dt + \mathbf{f}(t), \tag{9}$$

$$\mathbf{\Omega} = [\dot{\mathbf{A}}, \mathbf{A}] \cdot \boldsymbol{\chi}^{-1}, \tag{10}$$

$$\mathbf{\Phi} = (\mathbf{f} \cdot \mathbf{f}(t)) \cdot \boldsymbol{\chi}^{-1}, \tag{11}$$

where $\mathbf{A}$ is the state vector whose components are given by the independent variables of the system, $\boldsymbol{\chi}$ is the static susceptibility tensor defined by

$$\chi_{ij} = \int_0^\beta \langle A_i e^{-\lambda H} A_j e^{\lambda H} \rangle d\lambda. \tag{12}$$

In the simple case of the random force with white spectrum, the time development of the averaged value of $\mathbf{A}(t)$ is given by[19]

$$\langle \dot{\mathbf{A}}(t) \rangle = (\boldsymbol{\gamma} \cdot \boldsymbol{\beta}) \langle A \rangle, \tag{13}$$

with

$$\boldsymbol{\gamma} = [\dot{\mathbf{A}}, \mathbf{A}] + (\mathbf{f} \cdot \mathbf{f}), \tag{14}$$

$$\boldsymbol{\beta} = \boldsymbol{\chi}^{-1}. \tag{15}$$

Once the linear equation of motion is established as above it is not difficult to obtain the spectral representation of the correlation function, $\varphi_{ij}(\omega) = \int \langle A_i(t) A_j(0) \rangle e^{i\omega t} dt$, in the form[20]:

$$\varphi_{ij}(\omega) = [\boldsymbol{\zeta} + i\omega\boldsymbol{\beta}]^{-1}_{ij} + [\boldsymbol{\zeta} - i\omega\boldsymbol{\beta}]^{-1}_{ij}, \tag{16}$$

$$\boldsymbol{\zeta} = \boldsymbol{\beta} \cdot \boldsymbol{\gamma} \cdot \boldsymbol{\beta}. \tag{17}$$

To apply the above general discussions to the present system, we define a five-component state vector:

$$\mathbf{A}^+ = (P_1(\mathbf{q}), Q_1(\mathbf{q}), P_2(\mathbf{q}), Q_2(\mathbf{q}), \sigma(\mathbf{q})), \tag{18}$$

where P_1, Q_1 are the momentum and the amplitude of the TO ($i = 1$) and TA ($i = 2$) phonons, and $\sigma(\mathbf{q})$ is the Fourier transformed pseudospin variable:

$$\sigma(\mathbf{q}) = 1/\sqrt{N} \int \sigma_i e^{i\mathbf{qr}} dr. \tag{19}$$

As stated above, we assume that the random force, which is acting only on the pseudospin variable has the white spectrum:

$$\langle f f(t) \rangle = \gamma \delta(t). \tag{20}$$

Physically, γ corresponds to the relaxation constant of the hopping motion of Pb^{2+}-ion.

The energy of the coupled TO-TA-spin system is expressed by,

$$\begin{aligned} H = \sum_{\mathbf{K}} \{ &\frac{1}{2}(P_1^2(\mathbf{q}) + \omega_1^2(\mathbf{q}) Q_1^2(\mathbf{q})) \\ &+ \tfrac{1}{2}(P_2^2(\mathbf{q}) + \omega_2^2(\mathbf{q}) Q_2^2(\mathbf{q})) + \tfrac{1}{2} J \mid \sigma(\mathbf{q}) \mid^2 \\ &+ f_{12} Q_1(\mathbf{q}) Q_2(-\mathbf{q}) + g_1 Q_1(\mathbf{q}) \sigma(-\mathbf{q}) \\ &+ g_2 Q_2(\mathbf{q}) \sigma(-\mathbf{q}) \}, \end{aligned} \tag{21}$$

where the last three terms give the linear couplings between the spin and phonons.

Using eq. (16), we obtain the phonon spectral density in the 5-component system as follows:

$$S(\mathbf{q}, \omega) = \sum_{i=2,4} [\boldsymbol{\zeta} + i\omega\boldsymbol{\beta}]^{-1}_{ii} + [\boldsymbol{\zeta} - i\omega\boldsymbol{\beta}]^{-1}_{ii}, \tag{22}$$

$$\boldsymbol{\zeta} = \boldsymbol{\beta} \cdot \boldsymbol{\gamma} \cdot \boldsymbol{\beta}, \tag{23}$$

where $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ are explicitly given (See Appendix) by,

$$\boldsymbol{\beta} = \frac{1}{k_B T} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \omega_1^2 & 0 & f_{12} & g_1\omega_1 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & f_{12} & 0 & \omega_2^2 & g_2\omega_2 \\ 0 & g_1\omega_1 & 0 & g_2\omega_2 & k_B T - J \end{pmatrix}, \tag{24}$$

$$\boldsymbol{\gamma} = \begin{pmatrix} 0 & -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma \end{pmatrix}. \tag{25}$$

Notice if we eliminate the fifth row and column from $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ tensors, the spectral density simply reproduces the 'hypothetical' phonon dispersions given in Fig. 2 :

$$S(\mathbf{q},\omega) = \frac{1}{\hat{\omega}_1^2(\mathbf{q})}\delta(\omega \pm \hat{\omega}(\mathbf{q})) + \frac{1}{\hat{\omega}_2^2(\mathbf{q})}\delta(\omega \pm \hat{\omega}_2(\mathbf{q})), \quad (26)$$

where $\hat{\omega}(\mathbf{q})$'s are the renormalized TO and TA phonon frequencies. In this context, the present treatment may be viewed as a natural extension of AHS formalism to include the pseudospin freedom of motion.

In order to visualize general characteristics produced by the coupling to pseudospin (stochastic) variable, we consider a simpler case of 'single TO phonon-pseudospin coupled system.' In this case, we can obtain rather simple analytic expression of $S(\mathbf{q},\omega)$ as follows

$$S(\mathbf{q},\omega) = \frac{2k_BT\gamma\omega_1^2 g^2}{\omega^2(\omega^2-\omega_1^2)^2 + \gamma^2\{g^2\omega_1^2 + J'(\omega^2-\omega_1^2)\}^2} \quad (27)$$

$$J' = k_BT - J \quad (28)$$

Similar formula was already given by Yamada et al..[21,22] It is worthwhile to notice that the profile of the TO phonon spectrum changes drastically as 'two peak $\rightarrow$ broad single peak $\rightarrow$ triple peak' when the relative magnitude of ω_0 and γ is changed as $\gamma \gg \omega_0 \rightarrow \gamma \sim \omega_0 \rightarrow \gamma \ll \omega_0$. (See Figs. 1∼3 in ref. 21). Hence, if the relaxation constant γ satisfies the condition: $\gamma \sim \hat{\omega}_{TO}(\mathbf{q}_0)$, the profile of spectral distribution should exhibit the 'waterfall'-like behavior around $\mathbf{q} \cong \mathbf{q}_0$.

Keeping these considerations in mind we use eq. (22) to calculate numerically the phonon spectral density distribution of PMN along [100]-direction in the region $0 \leq q \leq 0.2$. The important parameter γ has been taken as $\hbar\gamma$ =7meV. The result is depicted in Fig. 5 (a), in comparison with the experimental results by Gehring et al.. In spite of that we have used only limited number of disposable parameters $(f_{12}, g_1(=g_2), \gamma)$ the characteristic features of the observed neutron spectrum through the whole $\mathbf{q}$-region has been well reproduced.

IV. CONCLUSIONS AND DISCUSSIONS

In conclusion, we have developed a theory to study the characteristics of dipolar / strain fluctuations in perovskite relaxors. In addition to the soft TO and TA phonons, we take into account another freedom of motion associated with the random hopping of Pb^{2+} ions between the off-center sites around the high symmetry corner site, thus constructing a coupled TO-TA-pseudospin model to describe the perovskite relaxors.

It is shown that there is a possibility that prior to the on-set of instability of the uniform TO-mode (soft-mode), instability of TA mode with nanometer scale modulation ($\mathbf{q} \sim 0.1\mathbf{a}^*$) takes place, which produces static heterogeneous structure concerning polarization as well as shear strain. In the case of PMN, the most probable direction of modulation is [110]-direction. This seems to suggest the intrinsic origin of the heterogeneity in relaxors visualized as random distribution of PNR.

The phonon spectral density distribution has also been investigated. It is shown that when the relaxation time of random hopping of Pb^{2+} ions between the equivalent off-center sites is comparable to the TO phonon frequency at $\mathbf{q} \cong 0.1\mathbf{a}^*$, the calculated phonon spectral density reproduces the characteristic features called 'waterfall' which was observed by neutron spectra in PMN and PZN.

In this paper, we have discussed the possible origin of intrinsic heterogeneity in relaxors in terms of TA mode instability. Since the energy is simply assumed in a quadratic form, the resultant heterogeneity is expressed by a harmonic modulation. When higher order terms are taken into account, the modulation would become more or less 'kink'-like producing well defined boundary between the polar and non-polar regions. Recently, Yamada and Takakura investigated the origin of IC phase and two-phase coexistence in $A_{0.5}B_{0.5}MnO_3$ (CMR substance) observed around metal-insulator phase boundary based on TDGL formalism. Without the higher order coupling between 3d-orbital of Mn^{3+} ion and local strain, the system stabilizes a regular IC structure. However when the higher order electron-phonon coupling is taken into account, a two-phase coexistent state is stabilized in which metallic nanoregion is embedded randomly on the parent insulator phase.

Similar features would be expected in relaxors. Particularly, the random distribution of B-site ions provides the random pinning center to fix the 'kink' (domain boundary) position, which will enhance the randomness of the spatial heterogeneity. This situation could explain the discrepancy between the observed and the calculated diffuse patterns around (h00)-type Bragg position as shown in Fig. 3.

Acknowledgments

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APPENDIX A

We start with general thermodynamical equation of motion of a mult-component variable $\mathbf{x}(=\{x_i\})$:

$$\dot{\mathbf{x}} = -\boldsymbol{\gamma}\mathbf{X}, \quad (A1)$$

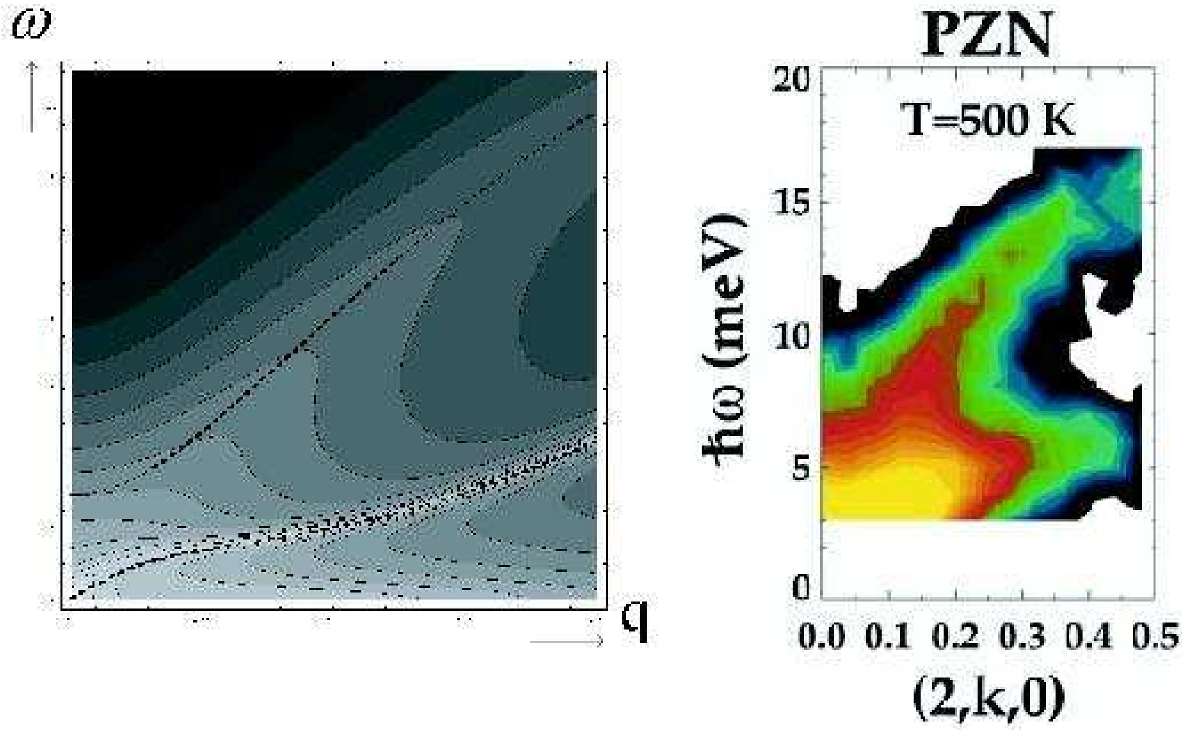

FIG. 5: (a) Calculated phonon spectral density distribution, $S(\mathbf{q},\omega)$, along [100]-direction in PMN, which is compared with the observed neutron scattering spectrum by Gehring et al.[7] reproduced in (b). The dashed lines corresponds to the 'hypothetical' phonon dispersions when the coupling to the pseudospin is neglected.

where $\mathbf{X}$ is the 'driving force' of the system defined in terms of the thermodynamical potential $F(\mathbf{x})$ given by

$$\mathbf{X} = \frac{1}{k_B T}\frac{\partial F}{\partial \mathbf{x}}. \tag{A2}$$

When F is given in the quadratic form with respect to $\mathbf{x}$ as,

$$F = \sum_{il} \beta_{ik} x_i x_l, \tag{A3}$$

X becomes the linear function of $\mathbf{x}$:

$$\mathbf{X} = \boldsymbol{\beta}\cdot\mathbf{x}. \tag{A4}$$

Substitution of (A4) into (A1) gives

$$\dot{\mathbf{x}} = -(\boldsymbol{\gamma}\cdot\boldsymbol{\beta})\mathbf{x}. \tag{A5}$$

Conversely, $\dot{\mathbf{X}}$ is expressed as

$$\begin{aligned}\dot{\mathbf{X}} &= -\boldsymbol{\zeta}\cdot\mathbf{x} \\ &= (\boldsymbol{\beta}\cdot\boldsymbol{\gamma}\cdot\boldsymbol{\beta})\mathbf{x}.\end{aligned} \tag{A6}$$

Using these linearized equations, the spectral representation of the two-time correlation function:

$$\varphi_{il}(\omega) = \int \langle x_i(t)x_l(t+\tau)\rangle e^{i\omega\tau} d\tau \tag{A7}$$

is expressed in terms of the coefficients $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$ as follows:

$$\varphi_{il}(\omega) = [\boldsymbol{\zeta} - i\omega\boldsymbol{\beta}]^{-1}_{il} + [\boldsymbol{\zeta} + i\omega\boldsymbol{\beta}]^{-1}_{li}. \tag{A8}$$

We further notice that when $\varphi_{il}(\omega)$ is integrated over ω, we obtain the instantaneous (same time) correlation as,

$$\begin{aligned}\int \varphi_{il}(\omega)d\omega &= \int \langle x_i(t)x_l(t+\tau)\rangle e^{i\omega\tau} d\tau d\omega \\ &= \langle x_i x_l\rangle = k_B T \boldsymbol{\chi}_{il}\end{aligned} \tag{A9}$$

where $\boldsymbol{\chi}$ is the static susceptibility tensor. It is shown that within the linear approximation the instantaneous correlation is given by,

$$\langle x_i x_l\rangle = [\boldsymbol{\beta}^{-1}]_{il}. \tag{A10}$$

In order to apply the above treatment to the present case, we consider that the long wave TA and TO phonons under consideration may be treated as thermodynamical variables. Using the energy given in eq. (21), the associated thermodynamical potential is expressed in a quadratic form;

$$F = \sum_q \frac{1}{2}(P_1^2(\mathbf{q}) + \omega_1^2 Q_1^2(\mathbf{q})) + \frac{1}{2}(P_2^2(\mathbf{q}) + \omega_2^2 Q_2^2(\mathbf{q}))$$
$$+\tfrac{1}{2}J_k \mid \sigma(\mathbf{q}) \mid^2 - kT \mid \sigma(\mathbf{q}) \mid^2 + f_{12}Q_1(\mathbf{q})Q_2(-\mathbf{q})$$
$$+g_1\sigma(\mathbf{q})Q_1(-\mathbf{q}) + g_2\sigma(\mathbf{q})Q_2(-\mathbf{q}). \qquad \text{(A11)}$$

As for the entropy contribution, we have only taken into account the configurational randomness of the pseudospin variables.

Finally we compare the fundamental equations (13), (14), and (15) in the text with (A5), (A9) and (A10), from which the expressions for $\boldsymbol{\beta}$-and $\boldsymbol{\gamma}$-tensors are deduced as given in eqs. (24) and (25).

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